



Driving forces for the weathering and alteration of silica in the regolith: implications for studies of prehistoric flint tools.

Médard Thiry, Paul Fernandes, Anthony Milnes, Jean-Paul Raynal

► To cite this version:

Médard Thiry, Paul Fernandes, Anthony Milnes, Jean-Paul Raynal. Driving forces for the weathering and alteration of silica in the regolith: implications for studies of prehistoric flint tools.. *Earth-Science Reviews*, 2014, 136, pp.141-154. 10.1016/j.earscirev.2014.05.008 . hal-01087918

HAL Id: hal-01087918

<https://hal-mines-paristech.archives-ouvertes.fr/hal-01087918>

Submitted on 28 Nov 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Please cite this paper:

Thiry, M., Fernandes, P., Milnes, A., Raynal, J. P. (2014). Driving forces for the weathering and alteration of silica in the regolith: Implications for studies of prehistoric flint tools. *Earth-Science Reviews*, p. 141-154, doi.org/10.1016/j.earscirev.2014.05.008.

Driving forces for the weathering and alteration of silica in the regolith: implications for studies of prehistoric flint tools.

Médard Thiry¹, Paul Fernandes², Tony Milnes³, and Jean-Paul Raynal⁴

¹ Mines-Paris-Tech, Géosciences, 35 rue St Honoré, 77305 Fontainebleau, France,
medard.thiry@mines-paristech.fr

² SARL Paléotime, 272 rue du Lycée Polonais, 38250 Villard-de-Lans, France,
paul.fernandes@paleotime.fr

³ Geology and Geophysics, School of Earth and Environmental Sciences, The University of Adelaide, South Australia 5005, arjamilnes1@bigpond.com

⁴ CNRS, UMR 5199 PACEA, 33405 Talence cedex, France and Department of Human Evolution, Max Planck Institut for Evolutionary Anthropology, Leipzig, Germany,
jpraynal@wanadoo.fr

Abstract

A range of geochemical and mineralogical factors trigger the weathering and influence the stability of various silica phases under near-surface temperatures and pressures. Based on current knowledge of the crystallochemical basis of silica behaviour in near-surface environments, the mineralogical and petrographical transformations of silica under weathering conditions in the regolith are reviewed using data from wide-ranging and detailed investigations of siliceous materials. Some of the investigations are of siliceous materials that evolved in near-surface environments over geological time and thus the weathering and alteration features are relatively clear and well expressed. Examples include weathering of tightly cemented sandstones, the formation of silica duricrusts (pedogenetic silcretes), and the weathering of flintstones. The various micromorphological and mineralogical forms of silica as determined by high resolution petrographic and electron-optical techniques can be related to geochemical and hydrological conditions in particular microenvironments. However, new studies have demonstrated that silica alteration and transformation mechanisms can also occur within prehistoric and historic time intervals. These are also described but are more difficult to observe, principally because of the microcrystalline character of the alteration phases and the infra-millimetric scale on which they develop.

Of many potential applications of knowledge about the near-surface alteration of silica in regolith materials and the environmental conditions under which it occurs, our studies can be used as a basis determining the provenance and post-disposal history of prehistoric flint tools and artefacts, in part to determine the source of the primary raw material, and secondly to test the integrity of archaeological excavations. We suggest that the mineralogical and petrographical characteristics of the cortex of the flint (specifically the recrystallization, dissolution and deposition of the silica phases, and the spatial arrangement of surfaces that have undergone successive transformations) are related to specific and identifiable weathering environments.

Keywords:

silica; weathering; solubility; recrystallization; flint; prehistoric artifacts;

1 Introduction

Rates of dissolution and precipitation of silica in weathering environments are relatively slow and few detailed investigations have been undertaken to document the outcomes of these alteration processes. Although the effective solubility of silica at room temperature was measured during the 1950's (Krauskopf, 1956; Siffert, 1967) it was twenty or more years before complementary studies were published (Marshall and Warakowski, 1980) to assist research on weathering, and there have been no data since!

Our studies undertaken over many years have examined the weathering of siliceous materials on many continents in order to illustrate the behaviour of forms of silica under different environmental conditions and go some way to explain the responsible mechanisms and the time frames in which they occurred. The alteration processes and outcomes are complex. The influence of variations that occur in microenvironments, for example the porosity of the siliceous material, the percolation rate of water through the material, and repeated mechanical shocks, are some key controls.

In this paper we review the mineralogical and micromorphological transformations of silica in regolith materials. Although these transformations have occurred in a geological time frame, new data has demonstrated that similar transformations of silica can occur much more quickly within prehistoric and historic time frames. Consequently, this information and the concepts derived may be applied in archaeological investigations where the provenance and post-disposal weathering and alteration history of prehistoric flintstone artefacts is a recurrent question. Some initial studies have been undertaken in this context.

2 Crystallo-chemical basis of silica behaviour

2.1 *Mineralogical forms of silica*

Under near-surface conditions silica forms several minerals that differ in the spatial ordering of silica tetrahedrons. Quartz is the most common silica mineral and forms at high as well as low temperatures. Chalcedony is a microcrystalline and fibrous variety of quartz (Drees et al., 1989). Moganite (Flörke et al., 1984; Rodgers and Cressey, 2001) is a widespread microcrystalline silica-mineral (Heaney and Post, 1992) but is not commonly identified in the descriptions of siliceous materials. Cristobalite and tridymite have a sheet-like crystalline structure (Correns and Nagelschmidt, 1933), similar to that of clay minerals, and in supergene environments they are often bound to chemical (evaporitic) deposits. Opal CT has also a sheet-like crystalline structure, with alternating cristobalite- and tridymite-like sheets (Flörke et al., 1975). It is relatively frequent in buried marine deposits and in confined continental environments. Opal is a petrographic variety of silica defined at the optical microscope level as amorphous because the crystallites are too small to be distinguished (Arbey, 1980; Folk and Weaver, 1952). It may correspond to true amorphous silica, but is most often composed of quartz, moganite, cristobalite, opal-CT, or a mix of these minerals. Amorphous silica has no crystalline organisation: silica tetrahedrons pile up in a disordered fashion and form chains limited to a few tetrahedrons.

2.2 Solubility of the various forms of silica

Silica in solution forms mono-molecular silicic acid $[\text{Si}(\text{OH})_4]$. The solubility of amorphous silica in water is about 120 mg/L SiO_2 and remains independent of the pH for values below 9 but increases strongly above 9 (Krauskopf, 1956). The solubility of all other silica varieties is lower than that of amorphous silica (Fig. 1). A fundamental law that rules geochemistry is that the most soluble phases sustain the precipitation of the less soluble ones. In this way, amorphous silica in equilibrium with a solution is able to sustain the crystallisation of every other crystalline silica variety, but these phases do not necessarily precipitate. Furthermore cristobalite, tridymite, chalcedony and all opal varieties are able to sustain the crystallisation of quartz (Garcia-Hernandez, 1981; Gislason et al., 1993; Iler, 1979; Siffert, 1967). Moreover, thermodynamic laws predict that as long as a more soluble phase is present, the less soluble phases do not dissolve, but kinetic dynamic equilibrium may partly disturb this rule. At room temperature the equilibrium between silica varieties and water is reached very slowly, sometimes only after 1 or 2 years (Dove and Nix, 1997; House and Hickinbotham, 1992; Siffert, 1967).

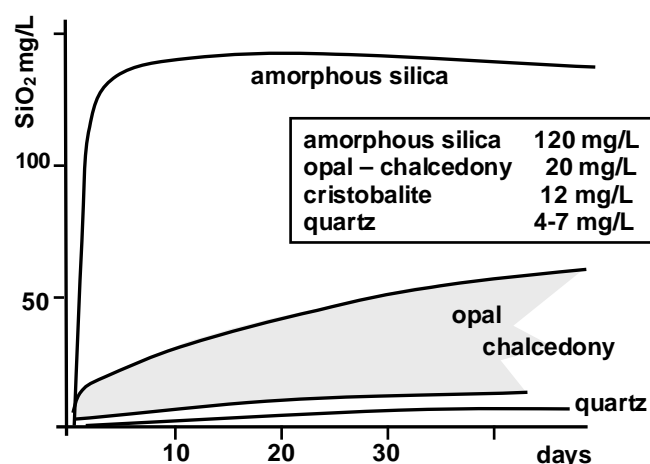


Figure 1 – Rate of dissolution and asymptotic solubility of the different silica varieties at 25°C (after Siffert 1967). The solubility equilibrium of the silica phases in water is reached slowly. Opal and chalcedony show variable solubility according to their respective crystallinity.

It should be noted that most ground waters around the world have silica content between 12 and 18 ppm SiO_2 (Garrels and Christ, 1965; White et al., 1963) that is roughly in equilibrium with clay minerals. This means that most groundwaters are oversaturated with respect to quartz (solubility 4-7 mg/L) and are thus potentially able to precipitate quartz. This oversaturation in silica with respect to quartz is thought to result from a kinetic dynamic equilibrium since the dissolution kinetics of clay minerals are much higher than those for the precipitation of quartz (Palandri and Kharaka, 2004).

It is possible to demonstrate a specific sequence of crystallization and particular relationships between the silica phases that form in surficial regolith environments. For example, siliceous duricrusts that have formed in soils (pedogenic silcretes) and occur over wide regions of the world display several distinct horizons with systematic micromorphological and mineralogical structures (Thiry, 1999). Detailed mineralogical and petrographic studies show that, consistently from the base to the top of the profile (Fig. 2):

opal → microcrystalline quartz → euhedral quartz

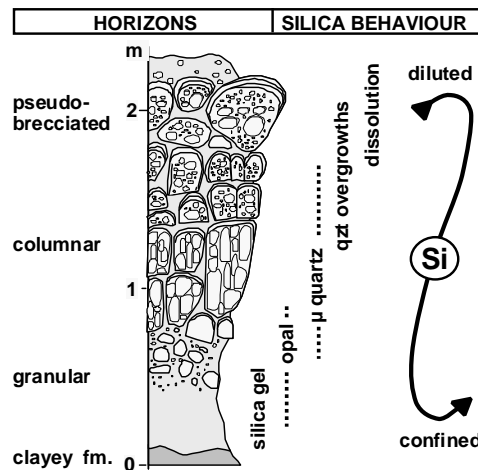


Figure 2 – Macro- and micromorphological structures of a pedogenic silcrete profile. The siliceous matrix is the location of successive silica dissolution and deposition leading to relative accumulation of crystalline quartz.

This distribution of silica phases reflects the chemistry of the solutions from which they precipitated (Williams and Crerar, 1985). Microcrystalline, amoebic and euhedral quartz in the upper horizons developed from dilute infiltrating soil water solutions that dissolved pre-existing more soluble silica phases. The leached silica migrated down towards the base of the profile and precipitated microcrystalline quartz as a result of the progressive concentration of silica in solution by evaporation. In this sequence, each mineralogical and petrographical silica species is derived from the previous generation by in-situ dissolution and recrystallization, indicating the re-equilibration of the mineral with its environment. The recrystallizations are irreversible and ultimately favour development of quartz (Thiry and Millot, 1987).

The influence of organic compounds (i.e. humic acids, oxalic acid, alkanes) on silica solubility in the regolith is poorly known and has been generally neglected in the past. Recent studies have shown that silico-organic complexes raise silica solubility and influence dissolution kinetics (Bennett, 1991).

Additionally, the influence of temperature on the solubility of quartz is important. Quartz solubility decreases exponentially with temperature (Rimstidt, 1997, Williams et al., 1985). Between 12.5 and 0°C quartz solubility decreases to half its initial value (Fig. 3).

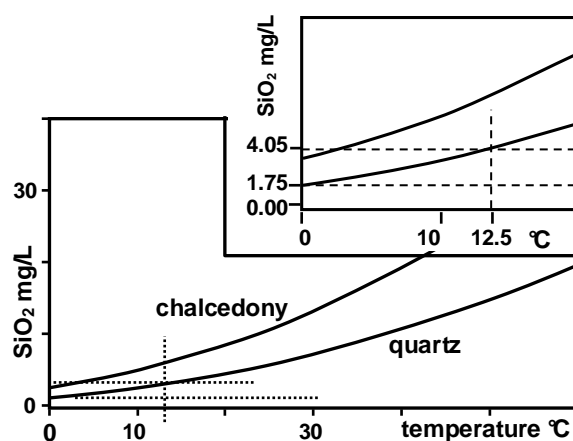


Figure 3 – Quartz and chalcedony solubility versus temperature (Bethke, 2002). Quartz solubility decreases to more than half of its initial value between 12.5 and 0°C.

2.3 Stability of forms of silica vs crystallinity

The crystallinity of the various forms of silica relates to the geochemistry of the solution from which they precipitated. Solutions with high silica content favour the blooming of crystal nuclei and crystal defects that restrict the growth of crystals and consequently amorphous or low crystallinity silica varieties will form (Lee, 2007a). On the other hand, in dilute solutions, the number of nuclei, as well as impurities, remains limited. As a consequence, elementary crystallites form regularly and large quartz crystals develop or, under less favourable conditions, microcrystalline or fibrous silica varieties are formed.

An empirical relation exists between the stability (the reverse of solubility) of silica varieties and their degree of structural order and crystallinity. Large silica crystals, which have few structural defects, are the most stable; for example euhedral quartz and quartz overgrowths on matrix grains. Silica varieties such as opal (formed of nanoquartz), microcrystalline quartz, moganite and fibrous silica varieties with numerous structural defects form small elementary crystallites (coherent crystal domains). They are relatively more soluble than quartz, in terms of thermodynamic solubility and kinetics (Gislason et al., 1993; Williams et al., 1985), and so the microcrystalline silica varieties, especially moganite, are preferentially dissolved in the first stages of weathering (Gislason et al., 1997) (Fig. 4).

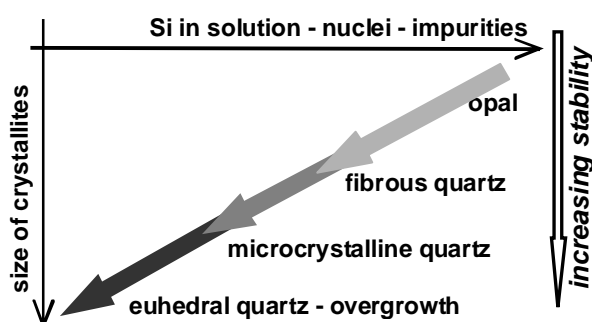


Figure 4 – Schematic relation between stability and crystallinity (size of the elementary crystallites) of the different petrographic varieties of quartz.

Silica solubility may even vary within a single crystal due to domains of various degrees of crystallinity: increased crystallinity correlates with a larger size of the coherent (without defect) domains of its atomic arrangement, or is inversely proportional to the frequency of crystal defects. The variation in crystallinity of quartz, for example, can be evaluated by several methods (Graetsch et al, 1987; Herdianita et al., 2000b; Lee, 2007a; Moxon et al., 2006; Murata and Norman, 1976; Smykatz-Kloss, 1972) including the full width at half-maximum intensity of an X-ray diffraction band, the intensity of peaks in X-ray diffraction patterns (quantitative analyses), and the sharpness/intensity of the thermal transformation of quartz- α into quartz- β as determined by Differential Thermal Analysis.

Detailed studies of the quartzite pans of the Fontainebleau Sandstones show the relationship between solubility and crystallinity. These pans are tightly cemented and have a friable rim that results from partial dissolution of the quartzite (Thiry, 1999). As clearly indicated in thin sections (Fig. 5), the dissolution preferentially affects overgrowth quartz aureoles: primary quartz grains are hardly ever corroded (Thiry et al., 1984). This contrasted dissolution behaviour highlights the occurrence of two different kinds of quartz crystals in the quartzite, although there appears to be no distinction between primary quartz grains and secondary quartz overgrowths in the optical microscope. The overgrowth quartz, which precipitated at low temperature within a near-surface water table, has a higher solubility than the inherited magmatic quartz grains, presumably because the former has a lower crystallinity and more structural defects than the primary quartz.

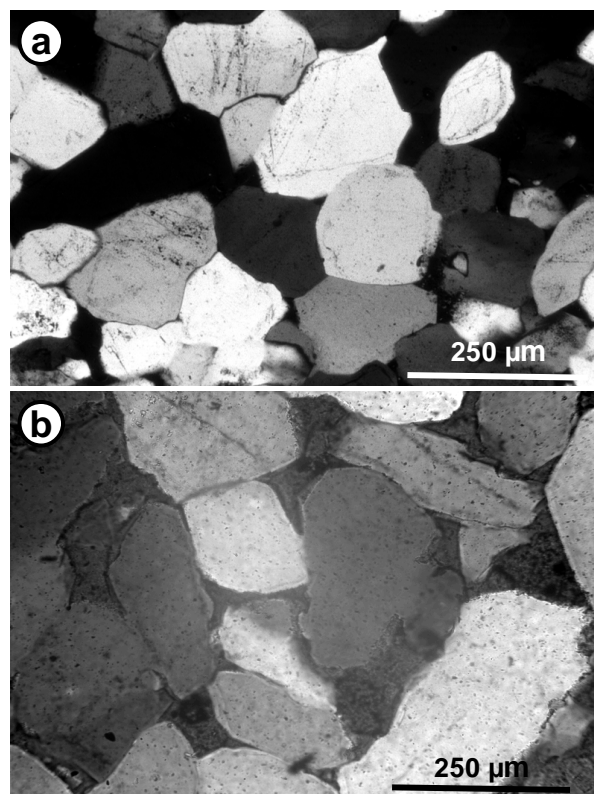


Figure 5 – Petrography of the Fontainebleau Sandstones. a – The quartzite pans are cemented by subeuhedral quartz overgrowths. b –The quartzite rims show preferential dissolution of the overgrowth aureoles, but the primary quartz grains are not corroded. Thin sections, cross-polarized.

It is widely observed in diagenetic and weathering environments that successive transformations of silica phases generally results in increasing crystallinity and decreasing solubility (Goldstein and Rossi, 2002; Graetsch and Grünberg, 2012; Knauth, 1979; Lee, 2007b; Willey, 1980; Williams et al., 1985). Once precipitated the silica crystal begins to increase in size, resulting in a decrease in surface defects and a more compact structure (Moxon et al., 2006).

3 Spatial and temporal aspects of weathering and alteration of silica in near-surface environments

In natural systems silica generally behaves in a much more complex way than in laboratory experiments. This is mostly due to the specific spatial distribution of the various forms of silica in relation to water flows and because weathering and alteration reactions occur according to changes in ground water (and soil water) chemistry and conditions. Thiry and his colleagues have undertaken detailed investigations of several examples of the development, weathering and alteration of siliceous materials in the regolith in Europe and Australia, focussing particularly on mineralogical and micromorphological features (Thiry, 1999; Thiry and Maréchal, 2001; Thiry and Milnes, 1991; Thiry et al., 1988; Thiry et al., 2006). Here we review two examples of weathering and alteration in France that illustrate the complex of spatial and temporal processes that seem to act together but in fact occur alternately.

3.1 *Weathering and alteration of silica in outcropping sandstones*

Numerous outcropping sandstones around the world show specific weathering features at their surface and provide invaluable information about weathering of siliceous materials (Willems et al., 2002; Wray, 1997; Young and Young, 1992).

For example, in outcrop, quartzite pans in the Fontainebleau Sandstone break down and yield quartzite blocks that progressively acquire rounded dome-like morphologies (Thiry, 2005; Thiry et al., 1984). The domal structures are often coated with a 0.5 to 2 cm-thick hardened silica crust (Fig. 6a). The crust is restricted to the top of the domes, and does not occur on lower parts or on overhanging surfaces. The crust appears in relief as a result of differential alteration at the periphery of the domes. Thin sections across this hardened silica crust show that quartz overgrowths on original grains are split off by tiny cracks filled by brown opal (Fig. 6b).

Polygonal groove patterns about 5 to 10 cm in diameter develop on the flanks of the domes and on overhanging surfaces (Fig. 6c). Such grooves are never observed in the silica crusts on the top of the blocks. The layout of the overhanging structures clearly indicates that they are related to a former soil that has been stripped off by erosion. Thin sections across the grooves show the development of large intergranular voids that are related to preferential dissolution of the quartz overgrowths (Fig. 6d & 6e) that occurred within the former soil.

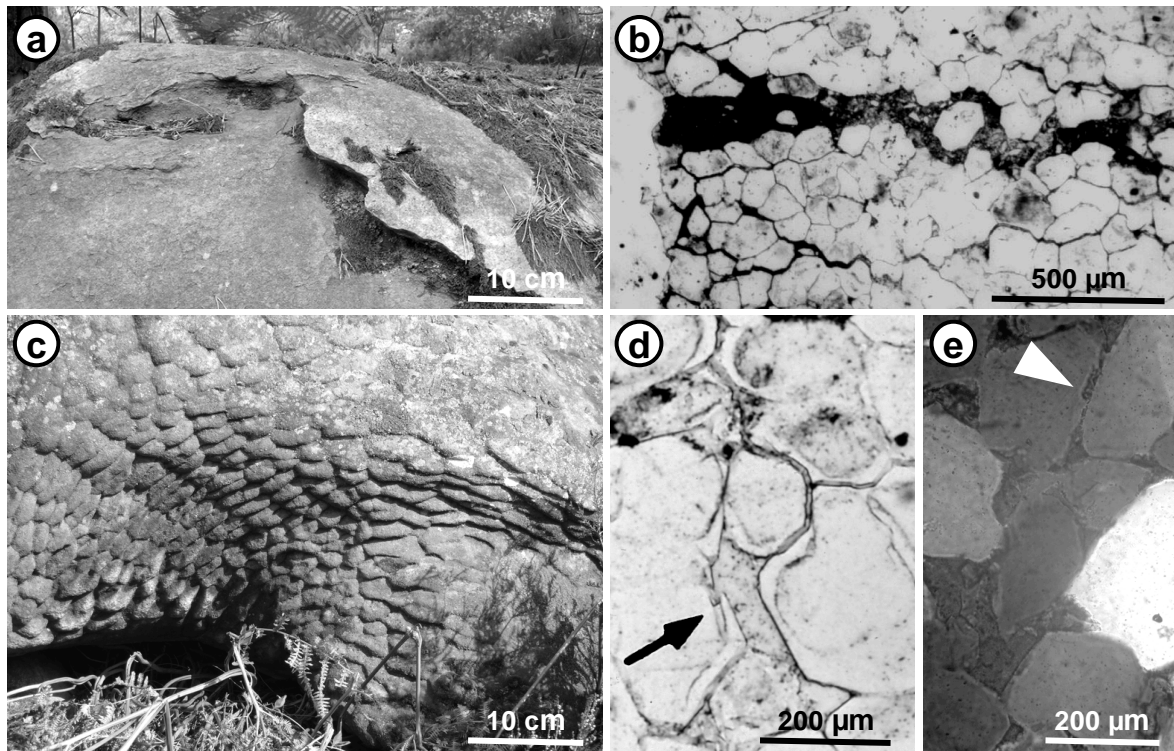


Figure 6 – Weathering morphologies of quartzite blocks. a - Dome-like shaped boulders capped with a silica crust. b - Brown opal deposits between dislocated quartz grains in the silica crust; thin section, polarized light. c - Polygonal network on a dome flank. d - Dissolution of quartz overgrowths along the polygonal grooves; thin sections, polarized light. e – Similar as d, with quartz wedge.

These typical quartzite weathering morphologies result mainly from concomitant and contrasted weathering processes, in particular silica dissolution and, to a lesser extent, silica deposition. It is important to recognise that even on the relatively small scale represented by individual quartzite domes, silica dissolution and precipitation do not occur in the same place or at the same time in weathering environments. Silica dissolution is enhanced on the flanks of the dome where there is contact with humid and organic-rich soils, and is probably due to complexation with organic compounds. Silica deposition occurs on the top of the domes and originates from pore waters from the quartzite blocks that are in equilibrium with quartz and which concentrate by evaporation during warm sunny days (Fig. 7). All quartzite blocks display these features, even those on very steep and unstable sandy slopes. Quartzite weathering is thus a current and rapid phenomenon and a millennium time scale (10 to 100 ka) is envisaged for its development as sandy slopes date back to the last glacial period (Thiry et al., 2010).

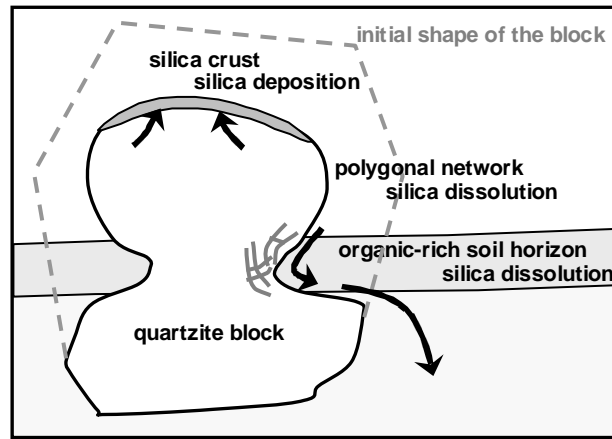


Figure 7 - Sketches of silica mobility during weathering of quartzite boulders. Silica dissolution is enhanced in contact with soils while silica deposition (opal) occurs at the top of the dome.

3.2 Weathering and alteration of silica in siliceous duricrusts

Siliceous duricrust profiles in France, Australia and elsewhere (Dubroeuq and Thiry, 1994; Thiry and Milnes, 1991; Thiry and Simon-Coinçon, 1996) display vertical and horizontal joints that determine their unique columnar structure (Fig. 8a). The voids linked to horizontal joints show specific features of successive reorganisation (Fig. 8b) (Thiry, 1981; Thiry and Millot, 1987). At the base of the joints silica accumulates in fine illuviation laminae. The youngest laminae, at the top, always consist of opal. The oldest laminae, at the base, commonly have a nodular structure and are formed of microcrystalline quartz. This sequence indicates a progressive recrystallization of the opal. The recrystallization is accompanied by a loss of silica which induces the destruction of the primary structures. The ceilings of the joints are lined with mammillary deposits of titania resembling stalactites. Preferential dissolution of microcrystalline quartz takes place in the ceilings of voids but coarse quartz grains are preserved and the resistant titania and impurity traces of the former microcrystalline quartz matrix have remained and accumulated in the mammillary deposits.

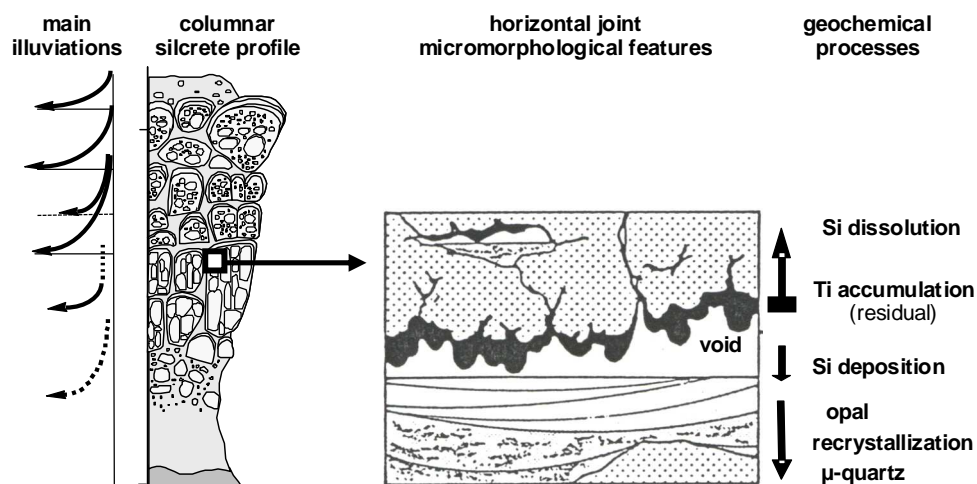


Figure 8 – The voids within columnar silcretes show Si dissolution in their ceilings (together with accumulation of residual titania), where water seeps through, whereas Si accumulates in form of opal in the base of voids, where solutions concentrate during dry periods.

The bases and ceilings of voids behave in different fashions according to the hydraulic regime. Opal deposits form in the base of the voids where water flows slowly or is stagnant and is concentrated by evaporation, while the microcrystalline matrix dissolves in the ceilings through which water seeps as a consequence of the percolation of soil water through the profile.

However, it is important to recognise that this close link between leached and confined environments does not imply a strict synchronism of degradation and construction. In fact, the two systems work alternately between humid (wet) periods during which silica dissolves and is leached downwards and dry periods during which the solutions that have accumulated at the base of the profile are concentrated by evaporation and opal crystallises. In between these fluctuations of the soil water regime, the secondary silica deposits may undergo partial dissolution, and successive dissolution-precipitation may trigger recrystallization into various microcrystalline petrofacies. Again, as in the studies of sandstone weathering and alteration, a complex of spatial and temporal conditions are implicated.

3.3 Influence of mechanical stress on weathering and alteration of silica

Prehistoric polishing features are known on numerous quartzite blocks in the Fontainebleau area (Hofstetter, 2004; Loiseau, 1970). They are polished abraded surfaces that are strikingly hardened and in relief, raised above the non-polished sandstone by weathering (Fig. 9a). This arrangement clearly points out that the “worked” surface is indurated and probably re-silicified. Such features are known world-wide on a variety of siliceous rocks used by prehistoric peoples. It is well known that rubbing surfaces together with a fine powder between them develops a “vitreous” film of amorphous character that coats the irregularities of the materials and gives the shiny aspect that is called the “Beilby layer” (Bowden and Hughes, 1937; Jones and Uehara, 1973). This amorphous film probably provides the silica for later recrystallization leading to hardening of the surface.

One of us (Thiry, unpublished work) has found that similar surface hardening is also developed on paving stones made of Fontainebleau quartzite. The paving stones can be found at several historical sites and show a convex surface due to wear (Fig. 9b). This surface is indurated with a millimetric crust that flakes off. Thin section studies show that quartz grains within the crust are intensely crushed and display microfractures spaced at about 10 μm and to a depth of 2 to 4 mm beneath the surface (Fig. 10a). This is the effect of repeated mechanical shocks. With such fractured grains one would expect that the exposed surface may be friable, but it is not. This is due to concomitant cementation and hardening as the microfractures have refilled with brown opal (Fig 10b & 10c). The opal has formed from silica dissolved from amorphous fracture edges in the crushed quartz and cements the quartz splinters together to form the hardened crust.

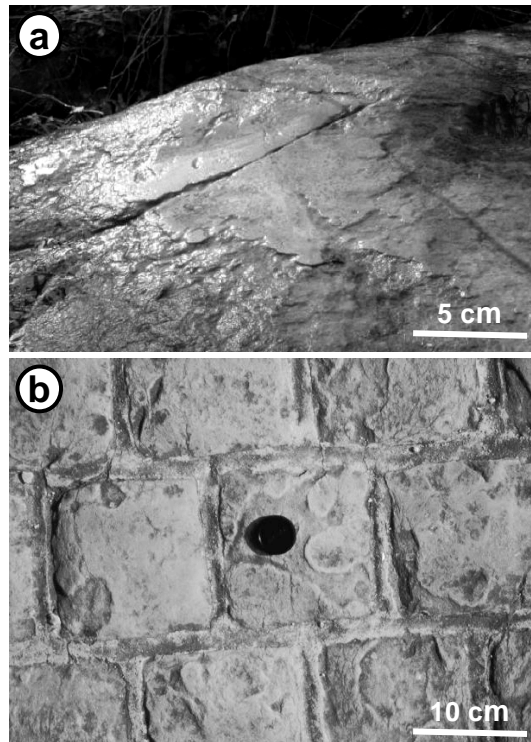


Figure 9 – Quartzite surfaces hardened by mechanical pressures. a – Indurated crusts of the "worked" surfaces of a Neolithic polishing stone, Fây-les-Nemours (Seine-et-Marne), Photo J.-P. Hofstetter. b - Paving stones made of Fontainebleau sandstone in an old barracks. Their abraded surface is hardened by a siliceous crust that flakes off.

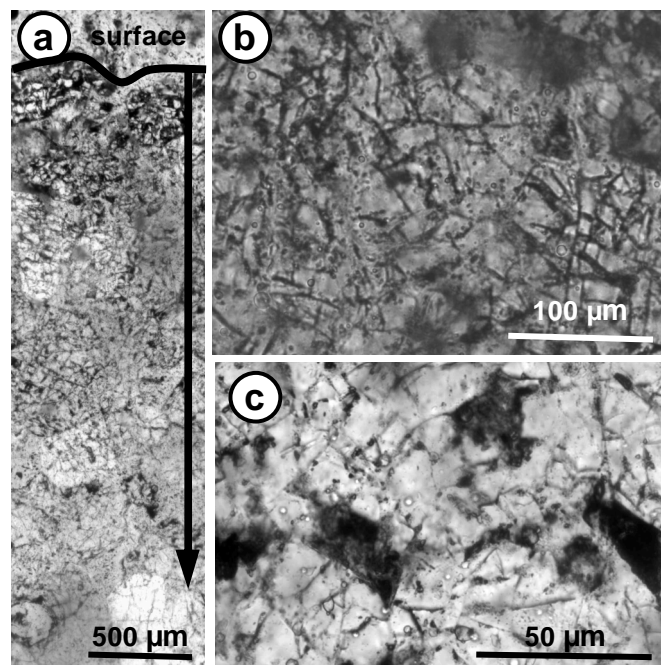


Figure 10 – Petrographic images of the hardened silica crusts developed on quartzite paving stones. a – Thin section perpendicular to the surface of the paving stone. Note the intense fracturing of the quartz grains at the surface and its progressive decrease with depth. b & c –Details of the fracturing of the quartz grains, showing 5 to 10 µm quartz splinters cemented by brown opal. Thin section, polarized light.

Whatever the crystallo-chemical mechanisms in detail, it is obvious that the mechanical shocks have had an effect on the quartz grains and that the hardening of the exposed surfaces can

occur within a few decades, as testified by the history of the paving stones. The development of an indurated crust on prehistoric polishing stones may have occurred in a similar time scale: although the polishing stones may have been used by several generations of prehistoric peoples, they were only used intermittently.

3.4 Weathering and alteration of silica in flintstones

The microcrystalline texture of flint makes it very difficult to observe and analyse its weathering and alteration in near-surface environments. Nevertheless, there are specific case studies of flint deposits that provide evidence of the geochemical and mineralogical mechanisms at play (Burroni et al., 2002; Bustillo et al., 2009; Catt, 1986; Glauberman and Thorson, 2012; Hurst and Kelly, 1961, Fayolle, 1979; Laignel and Meyer, 2000; Rodgers et al., 2004; Rottlander, 1975).

3.4.1 Alteration after reworking of flint from chalk deposits

A comparison of more than a hundred samples of flints in-situ within chalk deposits, and a similar number of samples of flints inherited in clay-with-flints and reworked into alluvium and sedimentary deposits, in France, was undertaken by Trauth et al. (1978). From a strict mineralogical point of view, flints embedded in chalk contain quartz as well as tridymite, cristobalite and opal-CT. These minerals are easily identified by X-ray diffraction and differential thermal analysis (Fig. 11). In contrast, flints reworked from chalk deposits and weathered are exclusively composed of quartz. In addition, all relevant indexes show that quartz in reworked flints is of higher crystallinity than quartz in flints embedded in chalk (Fig. 12).

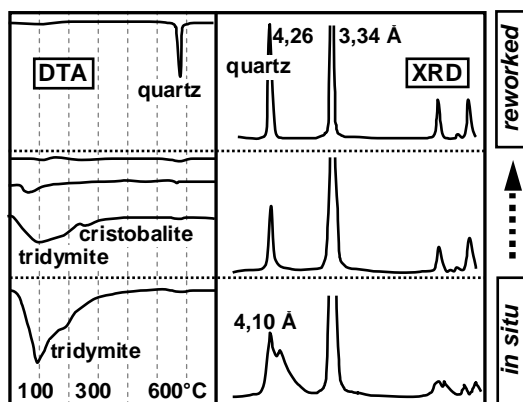


Figure 11 – Mineralogical composition of flints embedded in chalk and those reworked from chalk and weathered. The reworked flints are always only composed of quartz, whereas other silica varieties coexist beside the quartz in the flints in-situ within chalk (after Trauth et al. 1978).

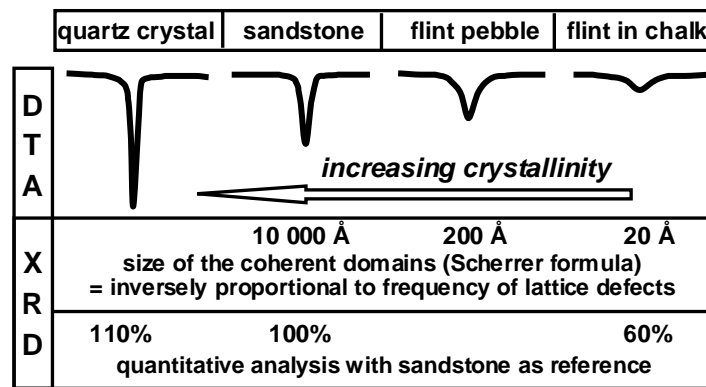


Figure 12 – The crystallinity of quartz (proportional to the size of the coherent crystal domains) is lower in the quartzose flints than in magmatic quartz. Moreover the reworked and weathered flints show quartz of a higher crystallinity than that in flints in-situ in chalk (after Trauth et al. 1978).

The mineralogical composition of flints starts to change after they are removed from the host chalk, even if the changes are not visible by means of petrographic techniques. The changes always favour a more stable secondary mineralogical structure, less soluble and of better crystallinity than the primary one. This process involves recrystallization triggered by the external environment of the flint and physico-chemical mechanisms like Ostwald ripening through which the smallest crystallites dissolve and contribute silica for the growth of larger crystals (Crerar et al., 1981). The mass balance exchange is minimal and there are no dissolution features. Recrystallization probably occurs through water films between the crystals and exchange by diffusion rather than by convection (Cady et al., 1996). Such recrystallization of silica phases may occur in a relatively short time as shown by primary opal deposits that have transformed to microquartz over periods of 20 to 50 000 years (Herdianita et al., 2000a).

3.4.2 Dissolution of flints

Often flint cobbles have a friable white cortex. Flints altered in this way are common at the top of clay-with-flints sections (Laignel and Meyer, 2000; Quesnel et al., 2003) and in fluvial terrace gravels (Coutard and Ozouf, 2008). Similar alteration affects some flint gravels interlayered in sand formations (Thiry et al., 1988). The friable white cortex is generally about 1 to 10 mm thick and the shape of the flint cobble is generally preserved. However, in some regolith environments the flints are more extensively altered and have contorted shapes (Fig. 13), with obvious solution features (cavities and hollows), and can be easily broken by hand. The friable white cortex is associated with progressive dissolution and development of porosity which may reach 35%, and a concomitant increase of the pore size and specific surface area, which may reach 15 m²/g in the most altered, powdery samples (Coutard and Ozouf, 2008).

These weathering features illustrate the sensitivity of the flints to silica leaching, with the progressive development of a friable white cortex. As reworked flints are primarily exclusively composed of microcrystalline quartz (in contrast with primary flints in chalk that contain some tridymite and cristobalite), the development of the friable texture reveals the preferential or relatively rapid dissolution of some of the microquartz varieties. These are most probably quartz microcrystals that have the lowest crystallinity and the smallest grain size (and thus the highest specific surface area). Once the dissolution has started, porosity develops, promoting water penetration into the flint and enhancing dissolution. The less soluble quartz microcrystals remain

and are preserved, or at least partly preserved. These have the greater grain size with less structural defects and thus better crystallinity.

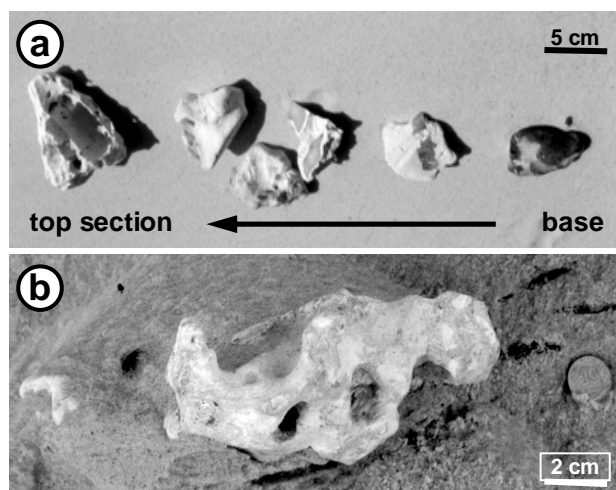


Figure 13 – a – Selected flints showing progressive alteration and dissolution from base to top of a bleached sandstone section (Thiry et al., 1988). b - Detail of an extensively altered flint from upper part of the section

A few occurrences of flint cobbles embedded in geological formations allow us to estimate the rate of development of the friable white cortex. In the Paris Basin, leached and bleached sandstone profiles that contain weathered flints are related to valley incision, and thus the duration of the alteration producing the cortex is probably several 10 ka (Thiry et al., 1988). Elsewhere, along the Channel shore in Normandy, flints with a thick, friable cortex are found in association with wave-cut platforms of Saalian and Eemian ages, and so the cortex is considered to have developed in less than 100 ka (Coutard and Ozouf, 2008).

3.4.3 Recrystallization of flints

Studies of geological formations that contain flints show that silica alteration and recrystallization phenomena occurred over long time periods. Weathering and alteration features no doubt occur in shorter time frames but are incipient and difficult to recognise.

Flint cobbles embedded in silcrete profiles of Lower Eocene age in the Paris Basin have been weathered and altered in-situ (Thiry, 1981; Thiry and Simon-Coinçon, 1996). In the upper parts of these silicified formations the flints show peripheral dissolution with a white and porous centimetric cortex and a dull core: only small primary translucent zones of the original flint remain. In thin sections the altered flints show microcrystalline quartz forming a microspherulitic texture with spherules about 10µm in diameter (Fig. 14). The microspherulites become more pronounced progressively from the core of the flint towards the cortex. Voids occur within the porous cortex and even larger voids can be observed at the outer rim.

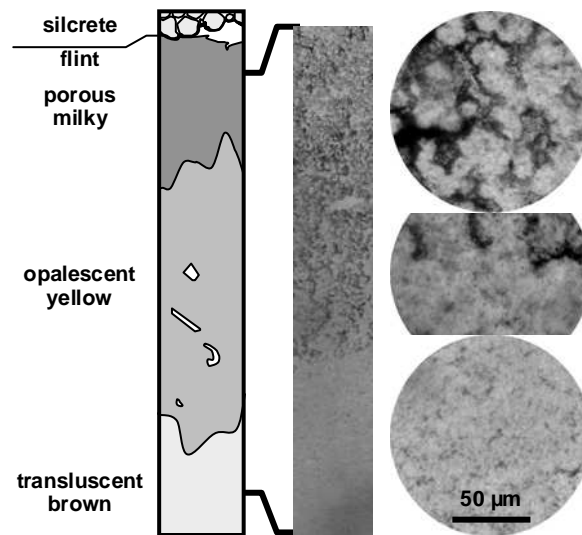


Figure 14 – Petrography of flint undergoing alteration in the upper part of a silcrete profile. Microspherulites become more distinctive through differential dissolution whereas they are not visible in the unweathered flint. Silica is in each case formed of very fine microcrystalline quartz.

The microspherulites are not visible in thin section in unweathered, translucent flints formed of very fine microcrystalline quartz. Nevertheless, it is obvious that these microspherulites are primary constituents of the flint. They have been described in fresh flints within chalk deposits (Cayeux, 1897; Knauth, 1994). The microspherulites become progressively more distinct because they have a lower solubility than the matrix between the spherulites that is composed of a different form of microcrystalline quartz, possibly mixed with opal, and that is more soluble and dissolves preferentially. These features reveal two successive transformations of silica in flints: (1) the presence of microspherulites show that recrystallization of the flint to microcrystalline quartz after it has been reworked from the chalk nevertheless preserved at least some of the primary petrographic features; and (2) weathering of flints results not only from simple dissolution processes but progresses as a result of differential dissolution and reorganisation of silica phases progressing from the surface inwards towards the core of the flints.

4 Application to investigations of flint artefacts

Determining the origins of lithic raw materials has long been considered essential to understand the collection behaviours of prehistoric societies. Petro-archeological studies of flints have difficulty in establishing a correlation between the artifact material and the potential sources of that material (Bressy, 2002; Briggs, 2001; Deflandre, 1935; Kars et al., 1990; Masson, 1981; Mauger, 1985; Sieveking et al., 1972; Valensi, 1957). Studies have been mostly on primary (in situ) and/or sub-primary sources, whereas gatherings of flints by prehistoric peoples were often probably made from secondary, redeposited materials such as glacial till and water-laid gravels (Fernandes and Raynal, 2006; Hughes et al., 2010; Lavin and Prothero, 1987, 1992; Verri et al., 2004; Williams-Thorpe et al., 1999). Transformations of the flint cortex that can be identified from detailed petrographic studies are specific to some sedimentary environments (Burroni et al., 2002; Fernandes, 2012; Fernandes et al., 2007; Hurst and Kelly, 1961). Recognition of these petrographic characteristics may be the key to characterizing secondary

flint deposits and could help to locate such deposits worked by prehistoric peoples and permit the drawing of maps of subsistence areas and potential itineraries (Fernandes et al., 2008).

As in the case of flintstones reworked from their sedimentary host, the silica minerals in flint tools made from flintstones and later buried when discarded by their users are affected by dissolution and precipitation (Fig. 15) (Arrighi and Borgia, 2009; Burrioni et al., 2002; Glauberman and Thorson, 2012; Hurst and Kelly, 1961; Masson, 1981; VanNest, 1985; Vignard and Vacher, 1964). Silica dissolution in flints buried within soils or sediments commonly occurs at the periphery due to water seeping through the surrounding material. On the other hand, silica precipitation may occur either by concentration of pore waters during dry periods (seasons), or by cooling of warmer groundwater rising to near-surface, for example at times of periglacial environments in Europe during the cold periods of the Quaternary (Woo et al., 2008).

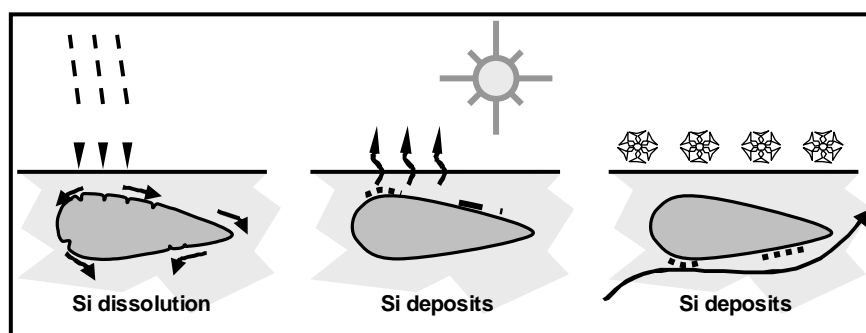


Figure 15 – Reworked or worked flints may undergo dissolution by seeping waters, but also be the focus of silica deposition by way of water concentration or cooling.

When transported flint clasts or worked tools are buried, a gradient of percolation is established between the essentially impermeable core of the flint and the host sediment or soil. Reactions within the margins of the flint occur via diffusion processes through water films between component silica crystals. Any primary interstitial water bound within the flint core will have had a long contact time with the silica minerals: in the outer rim, which is in contact with percolating water in the surrounding soil or sediment, the contact time will be shorter. This equates to a gradient of silica concentration in the solutions. Whereas the interstitial solutions and the water films between crystals within the core of the flint are in equilibrium with the silica minerals and no mineralogical change occurs, solutions at the surface of the flint are renewed by percolation and are thus undersaturated in silica so that the silica phases in the flint are dissolved. Beneath the surface layers of the flint, in the zone termed the cortex, solutions have intermediate silica concentrations that may trigger recrystallization (Fig. 16). Flint weathering always leads to a loss of silica. However, in turn, the crystallinity and therefore stability of the silica minerals increases, leading to more stable phases.

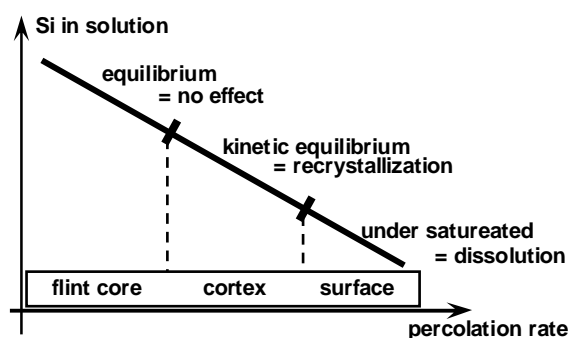


Figure 16 – Relationship between solution concentration and rate of percolation through the flints. Interplay between the flow rate of the solutions and their silica concentration steers the mineralogical and petrographical transformations in the flint cortex.

Of particular importance in unraveling the petrographic evolution of flint tools in near-surface environments in relation to the geochemical and kinetic behaviour of silica minerals is recognition of the remnant natural surfaces that are inherited from the primary chalk deposits. The detailed characteristics of these natural surfaces will reflect the environments in which the flints were deposited and contained before they were collected for tool-making. The first step in determining the provenance of flints is to decipher the spatial arrangement of the successive natural surfaces (flat surfaces, edges, depressions, cupules, etc) and their relative chronology (Fig. 17). Secondly, the wear marks and the neo-cortex formed when the sample was exposed, removed and transported have to be characterized for each surface. This requires a multi-scale approach by macroscopic and binocular observations, then examination of the microfacies, textures and porosity by optical microscopy, and finally a clarification of various phases of the silica dissolution and precipitation by scanning electron microscopy (SEM) (Fernandes, 2012).

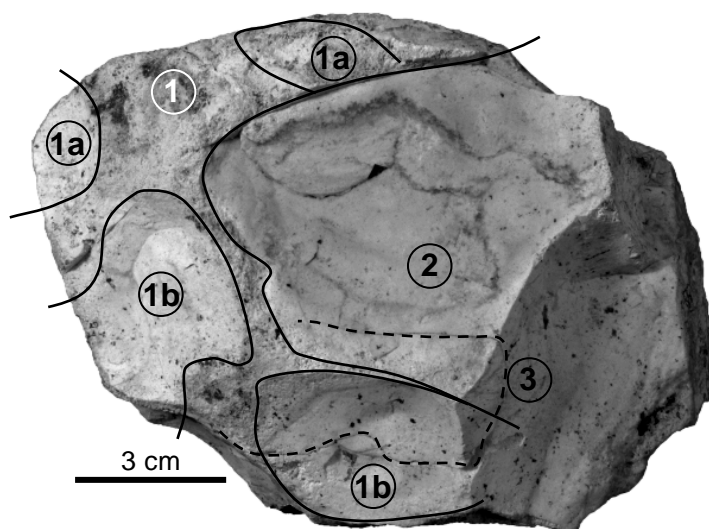


Figure 17 – Spatial arrangement of the successive surfaces on a flint cobble. (1) Primary flint cortex; (1a) and (1b) early cupulae with neo-cortex; (2) later cupula with a more recent neo-cortex; (3) recent developing cryojoint.

4.1 Pre-gathering weathering and alteration

Successive cortex transformations occur during the geological reworking process, for example in flints from colluvial deposits downslope from flint-bearing limestone outcrops and, further downstream, flints bound within a mature alluvial conglomerate. Studies so far have been undertaken on about 3500 flint cobbles and 8000 flint artefacts, and included 200 thin sections, and Scanning Electron Microscope analysis of 80 specific samples originating mainly from Massif Central, Rhône Valley and Aquitaine Basin in France and from several sites of Morocco (Fernandes, 2012).

The first stage of alteration after release of the flint from the source limestone consists of the development of three differentiated zones within the cortex (Fig. 18a). An inner micro-porous zone develops as a result of dissolution of the most soluble and less crystalline phases (diverse opal). An outer friable cortex with large pores develops with further dissolution. In between, a tight zone cemented by secondary crystalline silica (mainly microquartz) has formed.

In colluvium, most of the surface of the flint is remoulded by a thin layer of silica underneath which quartz grains remain visible (Fig. 18b & 18c). The silica layer is thicker in surface depressions and frequently shows shrinkage cracks. The most soluble mineral phases like calcite and opal CT have disappeared from the matrix of the flint. The cortex of the flint contains secondary silica deposits, abrasion on bulges and split features (Fig. 18d).

This complex weathering ultimately ends in the development of a thick silica layer that completely changes the surface of the flint. The cortex becomes smooth and the grains that form the flint underneath the silica layer are no longer visible. Sometimes, the silica coats biogenic elements, like diatom frustules, that record deposition in a quiet environment.

The development of silica coatings appears to be characteristic of flint weathering. It is a consequence of differential alteration: the most soluble silica phases are dissolved whereas more stable phases and of better crystallinity than in the primary one are preserved and/or precipitated (Graetsch and Grünberg, 2012). The silica coating remains partial and discontinuous on flints contained within colluvium. It thickens up and the flints become somewhat rounded in downgradient fluvial networks, until they become cemented entirely as well rounded pebbles in alluvial conglomerates. There appears to be a relationship between the thickness of the silica coating and the intensity and duration of the weathering and reworking processes. It is possible that mechanical stresses due to repeated friction, abrasion and impact of the flints during fluvial reworking gave rise to amorphous silica that has reorganised into silica coatings that harden the surface of the pebbles, in a similar way to that demonstrated above in paving stones and grinding stones.

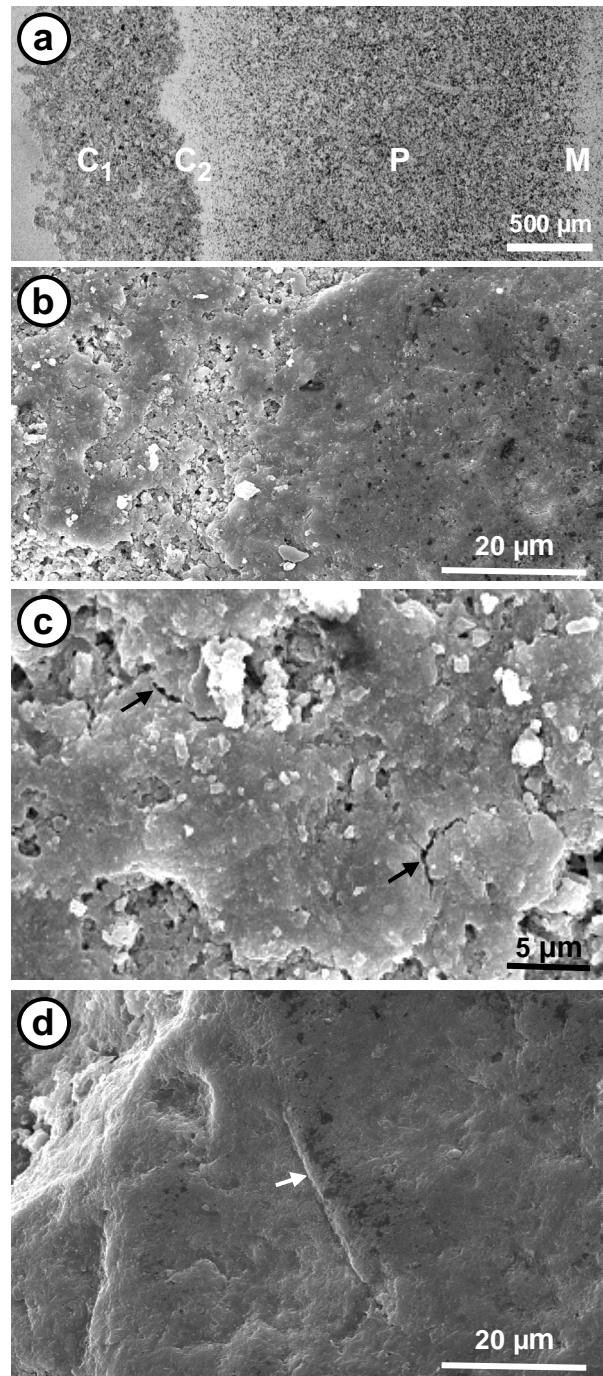


Figure 18 - Neo-cortex on reworked flints. a – Section from flint cortex in colluvial deposit (Cruas, Ardèche, France): (C1) Porous outer zone, microquartz with pore diameters up to 100 µm; (C2) tightly cemented zone, mainly composed of microquartz; (P) porous inner zone with dissolution of finest silica matrix and preservation of microquartz and chalcedony (bioclasts); (M) flint matrix without porosity, very fine silica phases including chalcedony and most probably poorly crystallized phases like varieties of opal and moganite. Thin section, cross polarized. b – Secondary silica coating in colluvial deposits (Cruas, Ardèche, France). Zone beneath the coating shows pores and granular texture typical of the outer zone of flint cores with dissolution and recrystallization of the more soluble silica compounds. c – Details of secondary silica coating with shrinkage cracks (arrows) resulting from loss of volume during transformation and dehydration of silica coating. Beneath is the granular and porous zone of the flint cortex. SEM picture. d – Tight silica coating on flint from alluvial deposit (Tertiary conglomerate from Naussac, Lozère, France). Thickness of coating seen in left upper corner of picture. A shock fracture affects the coating (arrow). SEM picture. After Fernandes (2012).

4.2 Alteration of worked flint flakes

The neo-cortex formed after knapping is the most demonstrative example of the alteration of flints. The alteration is obvious and can be dated, which allows an assessment of its rate of development. The alteration may also indicate the sedimentary and climatic processes that acted on the archaeological unit. Most commonly there are three zones superposed from the surface to the interior (Fig. 19): (1) an outer tightly cemented rim of a few tens of microns thickness, without porosity, which consists of a film of secondary silica that coats the microquartz and blurs entirely the granularity of the matrix; (2) a more or less regular underlying zone formed of microquartz without fibrous silica phases (chalcedony) that has relatively highly interconnected porosity and; (3) an inner zone in which the primary fibrous texture of chalcedony is preserved.

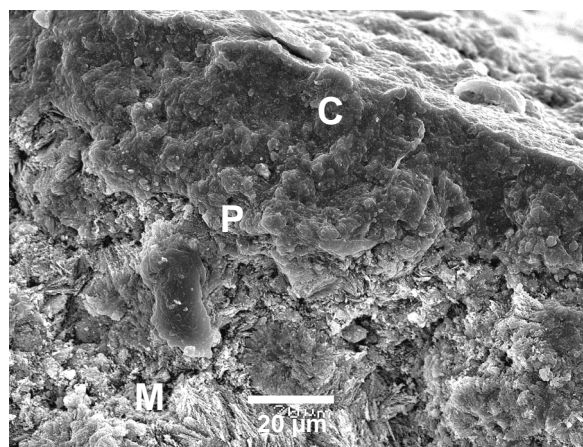


Figure 19 - Neo-cortex (C) tightly cemented by secondary silica without any granulation, overlaying a porous and granular zone formed of isometric microquartz (P) that developed above the primary flint matrix in which the lengthening textures of chalcedony remain (M). Section of a neo-cortex from an artefact worked from a Lower Cretaceous (Barremian) flint (Cruas, Ardèche, France). SEM picture after Fernandes (2012).

These neo-cortex alterations are frequent on flint flakes and are always characterised by a very fine silica phase covering the microquartz of the matrix. This is separated from the primary flint matrix by a network of open pores that indicates dissolution and recrystallization of the matrix as testified by the disappearance of the fibrous silica phases in the primary flint facies. This zonal arrangement may not have developed simultaneously but possibly successively or even in alternative fashion. The outer silica casing has most probably developed from amorphous silica compounds resulting from the knapping of the flints, or later mechanical shocks.

4.3 Implications

Weathering and alteration of silica in regolith environments has specific relevance to studies of the alteration of flint tools in near-surface environments. In particular, interpretations of the geochemical and kinetic behaviour of the constituent silica phases permits the forecasting of changes that may occur at the surface of a flint during its history (Fig. 20). For example: (1) dissolution always occurs at its surface; (2) percolation rates of soil water or groundwater through the core are very slow, and changes probably occur over geological time-scales (Ma);

and (3) the intermediate zone (sub-cortical zone) is the site of adjustment between the flint and its surrounding geochemical environment. Here, recrystallization and ultimately deposition of silica record the various environmental conditions experienced by the flint during its history and can be interpreted and characterised using petrographical and micromorphological techniques to provide clues to the source of the worked flint materials.

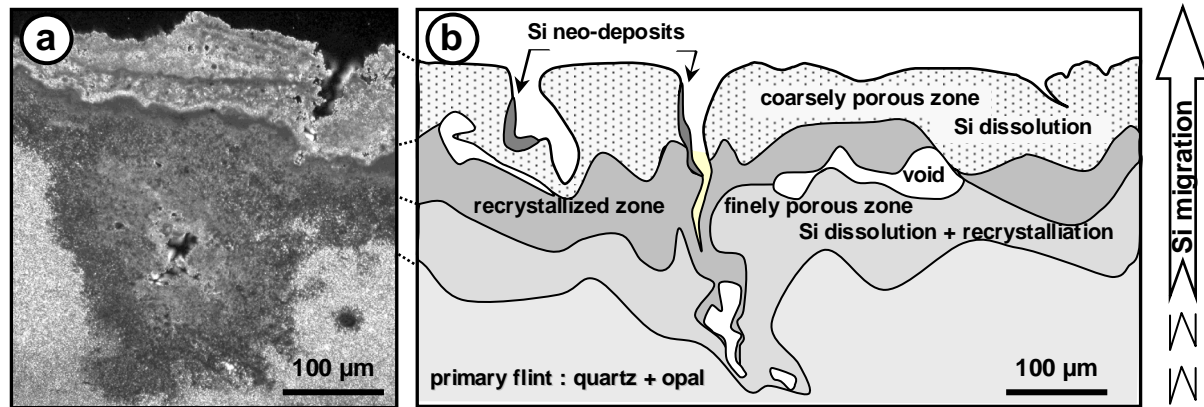


Figure 20 – Conceptual sketch of changes in the sub-cortical zone of flint. These changes are consequent upon the geochemistry of the pore water in the host sediment and provide the basis for reconstructing these environments. a – Thin section of cortex on flint from colluvial deposit (Cruas, Ardèche, France). b - Conceptual sketch of the petrographic changes that occur in a cortex of a flint during alteration.

Flint alteration and cortex development are mainly triggered by the nature of the component silica phases that have differing solubilities. The most soluble phases dissolve first and at the highest rate resulting in relative accumulation of the most stable phases. This is the first process of alteration. The crystallinity of the silica phases also plays a main role: it controls solubility which decreases with increasing crystallinity. Significant parts of the alteration process are the recrystallizations that occur in the solid state via diffusion in water films between crystal grains. Silica solubility is also temperature dependent: if groundwaters rise to the surface during cold periods they may precipitate silica and re-silicify cortex textures as they cool down.

The chemistry of interstitial water depends on the host material and on the water flow regime. In soils and in the zone of aeration, percolating water always remains under-saturated due to the low kinetic rate of silica dissolution: consequently dissolution will prevail during flint alteration. Groundwaters generally have a higher silica content and may be saturated with respect to the quartz varieties: dissolution of flint cortices will be limited in these environments. In clay-rich host rocks, such as clay-with-flints, percolating water flow rates are reduced and the silica content of the pore waters is even higher, favouring deposition of secondary silica.

Specific flow rates and water chemistry may be ascribed to sedimentary characteristics of flint deposits. For example, colluvium on slopes has intermittent drainage. Young alluvium may be permanently drowned whereas old alluvium may have the form of emerged terraces and undergo silica leaching for long periods. Flints at the soil surface, constituting an easy supply of materials, are exposed to severe temperature changes, desiccation, overheating in the sun, and exposure to the winds, and may undergo very specific alterations. Leaching conditions may even be different between the upper and the lower faces of a flint: the upper faces may undergo

leaching but may also be subject to silica precipitation when the percolation rate slows down or even stops, whereas the lower faces always experience outflows and thus leaching conditions.

5 Conclusions

High resolution petrographic and electron optical investigations of weathering and alteration of the various forms of silica in materials that are exposed to near-surface regolith environments provide the basis for assigning micromorphological and mineralogical features to geochemical and hydrological conditions in particular micro-environments. The materials studied over many years and on several continents include sandstones, siliceous duricrusts, and flintstones. Where the weathering and alteration of silica occurs over geological time, as in the case of siliceous duricrusts, or a millennium time scale, as in the case of the Fontainebleau Sandstone, features are generally clearly observed and comparatively easily interpreted. However, the weathering of silica can be a relatively rapid and current phenomenon. In the case of flintstones, there are examples of transformations of silica that occurred over periods of 20,000-50,000 years, thick weathering cortices have developed in less than 100,000 years, and friable cortices have formed in several decades. In addition, we describe examples of polishing and surface hardening of rock surfaces initiated by abrasion and repeated mechanical working followed by subsequent silicification that has occurred within a few decades. Details of the alteration features produced over shorter time periods are progressively less easily examined. However, the outcomes of studies of these alteration features can be used to investigate the provenance of flint tools in an archaeological context.

As well as flintstones, worked flint flakes exhibit various cortices and patinae that are due to changes in the texture and mineralogy at their surface forced by physico-chemical exchanges during working and weathering. And, as in the case of our geological and mineralogical studies in regolith environments, the textures (component particles, geometric aspects, size, mutual relations among the components, granularity) of the cortex and patinae result from changes that occurred under specific microenvironmental conditions and thus reflect evidence of these conditions. Firstly, the remnant primary cortex of flint tools may provide information that identifies the deposits from which prehistoric peoples obtained the flints. Secondly, worked flint flake cortices retain information that may aid in the reconstruction of the environment of the archaeological site and indicate if the artefacts may have been reworked or not. An inventory of flint cortex textures forms the basis for elucidating the mechanisms that triggered the formation of the textures. Three main influencing factors are the nature of the silica components, the pore water of the host sediments or soils and water flow or percolation regimes. Each flint registers its own history, and each type of environment lays down certain characteristic features on its surface, so that morphological and mineralogical changes recorded in the flint cortex can be used to reconstruct the successive environmental conditions experienced by that flint. Thus, a flint flake is not only a petrographical and archaeological entity; it also wears clues of alterations that, once deciphered, potentially reveal a chronology of sedimentary, diagenetic and archaeological events.

Acknowledgements: Research on prehistoric artefacts from different sites of the Massif Central and field surveys were funded by the Ministère de la Culture et de la Communication and the Région Aquitaine (project Origines). The laboratory CRP2A-IRAMT, UMR 5060 CNRS of the University Bordeaux 3, Esplanade des Antilles, F33607, is thanked for access to their SEM facilities. Christine Franke from Mines-ParisTech is acknowledged for comments of an early version of the manuscript.

References

- Arbey, F., 1980. Les formes de la silice et l'identification des évaporites dans les formations silicifiées. *Bull. Centre Rech. Pau. SNPA*, 4(1), 309-365.
- Arrighi, S., Borgia, V., 2009. Surface modifications of flint tools and their functional meaning. *Materials and Manufacturing Processes*, 24(9), 922-927, doi:10.1080/10426910902987150
- Bennett, P.C., 1991. Quartz dissolution in organic-rich aqueous systems. *Geochimica et Cosmochimica Acta*, 55, 1782-1797.
- Bethke, C.M., 2002. The geochemist's workbench release 4.0: a user's guide to Rxn, Act2, Tact, React, and Gtplot. *University of Illinois, Urbana, IL*.
- Bowden, F.P., Hughes, T.P., 1937. Physical properties of surfaces. IV. Polishing, surface flow and the formation of the Beilby layer. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 160(903), 575-587.
- Bressy, C., 2002. *Caractérisation et gestion du silex des sites mésolithiques et néolithiques du Nord-Ouest de l'arc alpin. Une approche pétrographique et géochimique*. Thèse de doctorat, Université Aix-Marseille I, 677 p.
- Briggs, C.S., 2001. The Past and Future of Irish Implement Petrography. *Ulster Journal of Archaeology*, 32-46.
- Burroni, D., Donahue, R.E., Pollard, A.M., Mussi, M., 2002. The surface alteration features of flint artefacts as a record of environmental processes. *Journal of Archaeological Science*, 29, 1277-1287.
- Bustillo, M.A., Castañeda, N., Capote, M., Consuegra, S., Criado C., Diaz-del-Río, P., Orozco, T., Pérez-Jiménez, J.L., Terradas, X., 2009. Is the Macroscopic Classification of Flint useful? A Petroarchaeological Analysis and Characterization of Flint Raw Materials from the Iberian Neolithic Mine of Casa Montero. *Archaeometry*, 51(2), 175-196.
- Cady, S.L., Wenk, H.R., Downing, K.H., 1996. HRTEM of microcrystalline opal in chert and porcelanite from the Monterey Formation, California. *American Mineralogist*, 81, 1380-1395.
- Catt, J.A. 1986. The nature, origin and geomorphological significance of clay-with-flints. in : Sieveking, G.D.G., Hart, M.B. (eds.), *The Scientific Study of Flint and Chert: Proceedings of the Fourth International Flint Symposium Held at Brighton Polytechnic 10-15 April 1983*. Cambridge University Press, 151-159.
- Cayeux, L., 1897. Contribution à l'étude micrographique des terrains sédimentaires. Deuxième partie : craie du Bassin de Paris. *Mém. Soc. Géol. Nord, Lille*, 4(2), 207-563, pl. IX et X.
- Correns, C.W., Nagelschmidt, G., 1933. Über Faserbau und optische Eigenschaften von Chalzedon. *Zeitschrift für Kristallographie*, 85, 199-213.
- Coutard, S., Ozouf, J.-C., 2008. Nouvelle approche de l'altération des galets de silex dans les dépôts marins pléistocènes : contribution à l'étude des plates-formes marines du Val de Saire (Normandie, France). *Quaternaire*, 19(4), 335-344.
- Crerar, D.A., Axtemann, E.V., Axtemann, R.C., 1981. Growth and ripening of silica polymers in aqueous solutions. *Geochimica et Cosmochimica Acta*, 45, 1259-1266.

- Deflandre, G., 1935. Techniques micropaléontologique appliquée à l'étude des silex. *Bulletin Société Française Microscopie*, 5(2), 76-79.
- Dove, P.M., Nix, C.J., 1997. The influence of the alkaline earth cations, magnesium, calcium, and barium on the dissolution kinetics of quartz. *Geochimica Cosmochimica Acta*, 61(16), 3329-3340.
- Drees, L.R., Wilding, L.P., Smeck, N.E., Senkayi, A.L., 1989. Silica in soils: quartz and disordered silica polymorphs. in: Dixon, J.B., Weed, S.B. (Eds), *Minerals in Soils Environments. Soils Sci. Soc. Am., Madison, Wisconsin*, 913-974.
- Dubroeucq, D., Thiry, M., 1994. Indurations siliceuses dans des sols volcaniques. Comparaison avec des silcrètes anciens. *15th World Congress of Soil Sciences, Acapulco, Mexico, July 10-16, Transactions*, 6a, 445-459.
- Fayolle, M., 1979. *Caractérisation analytique d'un profil à silex de l'ouest du Bassin de Paris*. Thesis 3rd Cycle, Univ. Paris VII, 151 p.
- Fernandes, P., 2012. *Itinéraires et transformations du silex : une pétroarchéologie refondée, application au Paléolithique moyen*. PhD Thesis, Université Bordeaux I, ED Sciences et Environnement, Spécialité Préhistoire, Vol. 1 Text and Figures 452 p, Vol. 2 Annexes 164 p.
- Fernandes, P., Le Bourdonnec, F.-X., Raynal, J.-P., Poupeau, G., Piboule, M., Moncel, M.-H., 2007. Origins of prehistoric flints: The neocortex memory revealed by scanning electron microscopy. *Comptes Rendus Palevol*, 6(8), 557-568. doi: 10.1016/j.crpv.2007.09.015
- Fernandes, P., Raynal, J.-P., 2006. Pétroarchéologie du silex: un retour aux sources. *Comptes Rendus Palevol*, 5(6), 829-837. doi: 10.1016/j.crpv.2006.04.002
- Fernandes, P., Raynal, J.P., Moncel, M.H., 2008. Middle Palaeolithic raw material gathering territories and human mobility in the southern Massif Central, France: first results from a petro-archaeological study on flint. *Journal of Archaeological Science*, 35, 2357-2370.
- Flörke, O.W., Flörke, U., Giese, U., 1984. Moganite. A new microcrystalline Silica-Mineral. *Neues Jahrbuch für Mineralogie, Abh.*, 149(3), 325-336.
- Flörke, O.W., Jones, J.B., Segnit, E.R., 1975. Opal CT crystals. *Neues Jahrbuch für Mineralogie Mh.*, 8, 369-377.
- Folk, R.L., Weaver, C.E., 1952. A study of the texture and composition of chert. *American Journal of Science*, 250, 498-510.
- Garcia-Hernandez, J.E., 1981. *Interprétation cinétique de la géochimie d'altération de la silice à basse température (25°C)*. INRA, Versailles, 213 p.
- Garrels, R.M., Christ, C.L., 1965. *Solutions, Minerals and Equilibria*. Harper and Row, New-York, 450 p.
- Gislason, S.R., Heaney, P.J., Oelkers, E.H., Schott, J., 1997. Kinetic and thermodynamic properties of moganite, a novel silica polymorph. *Geochimica et Cosmochimica Acta*, 61(6), 1193-1204.
- Gislason, S.R., Heaney, P.J., Veblen, R.R., Livi, K.J.T., 1993. The difference between the solubility of quartz and chalcedony: The cause? *Chemical Geology*, 107, 363-366.
- Glaubergerman, P., Thorson, M., 2012. Flint patina as an aspect of "Flaked stone taphonomy": A case study from the loess terrain of the Netherlands and Belgium. *Journal of Taphonomy*, 10(1), 21-43.
- Goldstein, R.H., Rossi, C., 2002. Recrystallization in quartz overgrowths. *Journal of Sedimentary Research*, 72, 432-440
- Graetsch, H., Flörke, O.W., Miehe, G., 1987. Structural defects in microcrystalline silica. *Physics and Chemistry of Minerals*, 14, p. 249-257.
- Graetsch, H., Grünberg, J. M., 2012. Microstruture of flint and other cherts raw material. *Archaeometry*, 54(1), 18-36. doi: 10.1111/j.1475-4754.2011.00610.x

- Heaney, P.J., Post, J.E., 1992. The widespread distribution of a novel silica polymorph in microcrystalline quartz varieties. *Science*, 255, 441-443.
- Herdianita, H.R., Browne, P.R.L., Rodgers, K.A., Campbell, K.A., 2000. Mineralogical and textural changes accompanying ageing of silica sinter. *Mineralium Deposita*, 5, 48-62.
- Herdianita, N. R., Rodgers, K. A., Browne, P. R., 2000. Routine instrumental procedures to characterise the mineralogy of modern and ancient silica sinters. *Geothermics*, 29(1), 65-81.
- Hofstetter, J.P., 2004. Les polissoirs de Fay-les-Nemours. web : http://home.nordnet.fr/jean-pierre.hofstetter/polissoirs.htm#_ftn7
- House, W.A., Hickinbotham, L.A., 1992. Dissolution kinetics of silica between 5 and 35°C. *Jour. Chem. Soc. Faraday Trans.*, 88, 2021-2026.
- Hughes, R.E., Högborg, A., Olausson, D., 2010. Sourcing flint from Sweden and Denmark A pilot study employing non-destructive energy dispersive X-ray fluorescence spectrometry. *Journal of Nordic Archaeological Science*, 17, 15-25.
- Hurst, V.J., Kelly, A.R., 1961. Patination of cultural flints: Flint artifacts can be dated by cortical changes in mineralogy and texture. *Science*, 134(3474), 251-256.
- Iler, R.K., 1979. *The chemistry of silica. Solubility, Polymérisation, Colloid and Surface Properties and Biochemistry*. John Wiley and sons, New York, 866 p.
- Jones, R. C., Uehara, G., 1973. Amorphous coatings on mineral surfaces. *Soil Science Society of America Journal*, 37(5), 792-798.
- Kars, H., Jansen, J.B.H., Virends, P., 1990. Petrography and geochemistry of flint from the Lanaye chalk (Rijckolt-ST. Geertuid) and some other Neolithic sources. *Cahier Quaternaire*, 17, 131-140.
- Knauth, L.P., 1979. A model for the origin of chert in limestone. *Geology*, 7, p. 274-277.
- Knauth, L.P., 1994. Petrogenesis of cherts. in: Heaney, P.J, Prewitt, C.T., Gibbs, G.V. (Eds.), *Silica, physical behaviour, geochemistry and materials applications. Mineralogical Soc. America, Reviews in Mineralogy*, 29(1), 233-258.
- Krauskopf, K.B., 1956. Dissolution and precipitation of silica at low temperature. *Geochimica et Cosmochimica Acta*, 10, 1-27.
- Laignel, B., Meyer, R., 2000. La désilicification des silex des formations résiduelles à silex de l'ouest du bassin de Paris. *Bull. Soc. géol. France*, 171, 569-576.
- Lavin, L., Prothero, D.R., 1987. Identification of Jasper Sources in Parts of the Northeast and Mid-Atlantic Region. *Bulletin of the Archaeological Society of New Jersey*, 42, 11-23.
- Lavin, L., Prothero, D.R., 1992. Prehistoric procurement of secondary sources: The case for characterization. *North American Archaeologist*, 13(2), 97-113.
- Lee, D.R., 2007a. Characterisation of silica minerals in a banded agate: implications for agate genesis and growth mechanisms. <http://www.geos.ed.ac.uk/homes/s0789516/agate.pdf>, 18 p.
- Lee, D.R., 2007b. Characterisation and the diagenetic transformation of non- and microcrystalline silica minerals. <http://www.geos.ed.ac.uk/homes/s0789516/microsilica.pdf>, 20 p.
- Loiseau, J., 1970. *Le massif de Fontainebleau. Géographie, histoire, généralités : légendes, préhistoire, géologie, faune, flore*. Vigot Frères Ed., Paris, 4th edition, 205 p.
- Marshall, W.L., Warakowski, J.M., 1980. Amorphous silica solubilities. II Effect of aqueous salt solutions at 25°C. *Geochimica et Cosmochimica Acta*, 44, 915-924.
- Masson, A., 1981. *Pétroarchéologie des roches siliceuses. Intérêt en Préhistoire*. Thèse Université Claude Bernard Lyon I, 111 p.
- Mauger, M., 1985. *Les matériaux siliceux utilisés au paléolithique supérieur en Ile-de-France*. Thèse de doctorat, Université Paris-1, 406 p.

- Moxon, T., Nelson, D.R., Zhang, M., 2006. Agate recrystallization: evidence from samples found in Archaean and Proterozoic host rocks, Western Australia. *Australian Journal of Earth Sciences*, 53, 235-248.
- Murata, K.J., Norman, M.B., 1976. An index of crystallinity for quartz. *American Journal of Science*, 276(9), 1120-1130. doi: 10.2475/ajs.276.9.1120.
- Palandri, J.L., Kharaka, Y.K., 2004. *A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modelling*. USGS, open file report n°2004-1068.
- Quesnel, F., Catt, J., Laignel, B., Bourdillon, C., Meyer, R., 2003. The Neogene and Quaternary Clay-with-flints north and south of the English Channel: Comparison of distribution, age, genetic processes and geodynamics. *J. Quaternary Science*, 18(3-4), 283-294.
- Rimstidt, J.D., 1997. Quartz solubility at low temperatures. *Geochimica et Cosmochimica Acta*, 61(13), 2553-2558.
- Rodgers, K. A., Browne, P. R. L., Buddle, T. F., Cook, K. L., Greatrex, R. A., Hampton, W. A., Herdianita, N.R., Holland, G.R., Lynne, B.Y., Martin, R., Newton, Z., Pastars, D., Sannazarro, K.L., Teece, C. I. A., 2004. Silica phases in sinters and residues from geothermal fields of New Zealand. *Earth-Science Reviews*, 66(1), 1-61.
- Rodgers, K. A., Cressey, G., 2001. The occurrence, detection and significance of moganite (SiO₂) among some silica sinters. *Mineralogical Magazine*, 65(2), 157-167.
- Rottlander, R., 1975. The formation of patina on flint. *Archaeometry*, 17 (1), 106-110.
- Sieveking, G.D., Bush, P., Ferguson, J., Craddock, P.T., Hugues, M.J., Cowell, M.R., 1972. Prehistoric flint mines and their identification as source of raw material. *Archaeometry*, 14(2), 151-176. doi: 10.1111/j.1475-4754.1972.tb00061.x
- Siffert, B., 1967. Some reactions of silica in solution: formation of clay. *Translation of: Mémoires du Service de la Carte géologique d'Alsace et de Lorraine, n°21, Published for the U.S. Department of Agriculture and the National Science Foundation, Washington, D.C.*, 100 p.
- Smykatz-Kloss, W., 1972. Das Hoch-Tief-Umwandlungsverhalten mikrokristalliner Quarze. *Contribution to Mineralogy and Petrology*, 36, 1-18. doi: 10.1007/BF00372830
- Thiry, M., 1981. Sédimentation continentale et altérations associées : calcitisations, ferruginisations et silicifications. Les Argiles Plastiques du Sparnacien du Bassin de Paris, *Sciences Géologiques Mém.*, 64, 173 p
- Thiry, M., 1999. Diversity of continental silicification features: Examples from the Cenozoic deposits in the Paris Basin and neighbouring basement. in: Thiry, M., Simon-Coinçon, R. (Eds), Palaeoweathering, palaeosurfaces and related continental deposits. *Spec. Publ. Intern. Ass. Sedimentologists*, 27, pp. 87-128.
- Thiry, M., 2005. Weathering morphologies of the Fontainebleau Sandstone and related silica mobility. *Ferrantia*, 44, 47-52.
- Thiry, M., Bertrant-Ayrault, M., Grisoni, J.C., 1988. Ground-water silicification and leaching in sands : Example of the Fontainebleau Sand (Oligocene) in the Paris Basin. *Geol. Soc. Am., Bull.*, 100, 1283-1290.
- Thiry, M., Maréchal, B., 2001. Development of tightly cemented sandstone lenses within uncemented sand: Example of the Fontainebleau Sand (Oligocene) in the Paris Basin. *Jour. Sedim. Research*, 71/3, p. 473-483.
- Thiry, M., Millot, G., 1987. Mineralogical forms of silica and their sequence of formation in silcretes. *Journal of Sedimentary Petrology*, 57(2), 343-352.
- Thiry, M., Milnes, A.R., 1991. Pedogenic and groundwater silcretes at Stuart Creek Opal Fields, South Australia. *Jour. Sediment. Petrol.*, 61(1), 111-127.

- Thiry, M., Milnes, A.R., Rayot, V., Simon-Coinçon, R., 2006. Interpretation of palaeoweathering features and successive silicifications in the Tertiary regolith of Inland Australia. *Journal of the Geological Society*, 163, p. 723-736.
- Thiry, M., Panziera, J.P., Schmitt, J.M., 1984. Silicification et désilicification des grès et des sables de Fontainebleau. Evolutions morphologiques des grès dans les sables et à l'affleurement. *Bull. Inf. Géol. Bassin Paris*, 21(2), 23-32.
- Thiry, M., Parcerisa, D., Liron, M.N., 2010. Periglacial geomorphological evolution of the Fontainebleau Massif (France). *Zeitschrift für Geomorphologie*, 54(1), 93–110.
- Thiry, M., Simon-Coinçon, R., 1996. Tertiary paleoweatherings and silcretes in the southern Paris Basin. *Catena*, 26(1), 1-26.
- Trauth, N., Vilas-Boas, G., Thiry, M., Badaut, D., Eberhart, J.P., 1978. Silex et chailles du bassin de Paris : modifications minéralogiques lors de leurs altérations. *Sciences Géologiques, Bull.*, 31(4), 173-183.
- Valensi, L., 1957. Micropaléontologie des silex du Grand-Pressigny. *Bull. Soc. géol. France*, 6(7), 1083-1090.
- VanNest, J., 1985. Patination of Knife River flint artefacts. *Plains Anthropologist*, 30(110), 325-339.
- Verri, G., Barkai, R., Bordeanu, C., Gopher, A., Hass, M., Kaufman, A., Kubik, P., Montanari, E., Paul, M., Ronen, A., Weiner, S., Boaretto, E., 2004. Flint mining in prehistory recorded by in situ-produced cosmogenic ¹⁰Be. *Proc. Nat. Acad. Sci. USA.*, 101(21), 7880–7884, doi: 10.1073/pnas.0402302101
- Vignard, E., Vacher, G., 1964. Altérations des silex préhistoriques de Nemours sous l'influence des climats qui se sont succédés du Périgordien Gravettien au tardenoisien locaux. *Bulletin de la Société Préhistorique Française*, 61(1), 45-55.
- White, D.E., Hem, J.D., Waring, G.A., 1963. *Chemical composition of subsurface waters*. in: . Fleischer, M. (Ed.), *Data of Geochemistry*, 6th ed., U.S. Geol. Survey Professional Paper 440-F.
- Willems, L., Pouclet, A., Vicat, J.P., 2002. Existence de karsts en roches cristallines silicatées non carbonatées en Afrique sahélienne et équatoriale, implications hydrologiques. *Bull. Soc. géol. France*, 17(3-4), 337-345.
- Willey, J.D., 1980. Effects of ageing on silica solubility: a laboratory study. *Geochimica et Cosmochimica Acta*, 44, 573-578.
- Williams, R., Crerar, D.A., 1985. Silica diagenesis. II General mechanism. *Journal of Sedimentary Petrology*, 55(3), 312-321.
- Williams, R., Parks, G.A., Crerar, D.A., 1985. Silica diagenesis. I. Solubility controls. *Journal of Sedimentary Petrology*, 55(3), 301-311.
- Williams-Thorpe, O., Aldiss, D., Rigby, I.J., Thorpe, R.S., 1999. Geochemical provenancing of igneous glacial erratics from southern Britain, and implications for prehistoric stone implement distributions. *Geoarchaeology*, 14(3), 209-246.
- Woo, M.K., Kane, D.L., Carey, S.K., Yang, D., 2008. Progress in permafrost hydrology in the new millennium. *Permafrost and Periglacial Processes*, 19(2), 237-254, DOI: 10.1002/ppp.613.
- Wray, R.A.L., 1997. A global review of solutional weathering forms on quartz sandstones. *Earth-Science Reviews*, 42(3), 137-160.
- Young, R.W., Young, A.R.M., 1992. *Sandstone landforms*. Springer-Verlag, 163 p.